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Specific heats of R_2Zn_{17} intermetallic compounds

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Abstract. Specific-heat measurements have been performed on polycrystalline R_2Zn_{17} compounds (R ≡ Pr, Nd, Tb, Dy, Ho, Er and Y) in the temperature range from 0.3 to 150 K. For all the compounds, except for R ≡ Y, magnetic anomalies in the specific heat have been observed, indicating the existence of magnetic order at low temperatures.

1. Introduction

In the past few years, much attention has been paid to the R_2T_{17} (R ≡ rare-earth element; T ≡ transition metal) intermetallics because of their relevant magnetic properties related to the R and T sublattice anisotropy (Franse and Radwanski 1992). A great deal of interest was focused mainly on the R_2Co_{17} compounds as candidates for use as permanent magnets because of their excellent anisotropic performances. The R_2Fe_{17} compounds turned out to be less interesting since they present magnetic order slightly above room temperature. After the discovery of the large influence that nitrogen absorption has on the magnetic order temperature (Hong Sun *et al* 1990), their possibility for practical applications is again being investigated. The isomorphous R_2Zn_{17} compounds have been found to be very interesting prototype systems to study in order to understand the anisotropic behaviour of the rare-earth sublattice, but information already reported is scarce. Pioneering work on some R_2Zn_{17} intermetallics was reported by Stewart and Coles (1974). Their results on the compounds with heavy-rare-earth ions in this series were not sufficiently extensive to elucidate the temperature of magnetic transitions as well as their anisotropic character. However, these workers definitively pointed out the antiferromagnetic character of the magnetic interactions in these compounds. In the R–Zn intermetallics, the Zn atom has no magnetic moment. In all the compounds, except Gd_2Zn_{17}, the R^{3+} ion has a paramagnetic moment close to the free-ion value (Stewart and Coles 1974). The relevant magnetic interaction is the indirect RKKY exchange between the R ions; as a consequence, very low ordering temperatures are expected. From magnetic susceptibility measurements performed from 2 K up to room temperature (Stewart and Coles 1974), a magnetic order transition was found only in the case of Gd_2Zn_{17} and Tb_2Zn_{17}. Inelastic neutron scattering experiments have been performed on the R_2Zn_{17} series (R ≡ Pr, Nd, Tb, Dy, Ho, Er and

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Y) over the temperature range from 3 to 100 K (Ibarra *et al* 1992) in order to obtain information about the crystalline electric field (CEF) experienced by the R ion. The energies and the transition probabilities of the observed CEF excitations were systematically analysed by fitting the experimental data, and a preliminary set of CEF parameters was deduced in the case of the Er^{3+} ion. In order to clarify the CEF level scheme and to confirm the reliability of these parameters, specific-heat measurements have been carried out on the R_2Zn_{17} compounds. As far as we know, no specific-heat measurements have been performed before. This technique is a very useful tool in the study of magnetic transitions and our results show the existence of antiferromagnetic order in all the measured rare-earth compounds. In this paper we report experimental results for several polycrystalline samples (R ≡ Pr, Nd, Tb, Dy, Ho, Er and Y) carried out in the temperature region between 0.3 and 150 K.

2. Experimental methods

Polycrystalline samples of R_2Zn_{17} were prepared by melting the high-purity metal components sealed in a molybdenum crucible. The samples were annealed for periods of 1 h at 1100 °C and 2 weeks at 850 °C; afterwards they were quenched in water. The R_2Zn_{17} compounds have two possible structural forms depending on the preparation temperature range (Iandelli and Palenzona 1967). In our case, only the high-temperature range was successful and, as a consequence, the samples have the rhombohedral Th_2Zn_{17} structure with space group $R\bar{3}m$. According to the x-ray pattern, the presence of secondary phases was not detected, at least in a content higher than 5%.

The specific-heat measurements were performed in the temperature range between 1.5 and 150 K by the adiabatic calorimetric method. The measurements from 0.3 to 4.2 K were carried out in a ^{3}He cryostat.

3. Experimental results and discussion

The analysis of the experimental results on the specific heat C takes into account the nuclear contribution C_n, the electronic contribution C_e, the lattice contribution C_{ph} and the magnetic contribution C_M, according to the expression $C = C_n + C_e + C_{ph} + C_M$.

The nuclear contribution to the specific heat has its origin in the interactions between the nuclear magnetic moment and the hyperfine field, and also in the interaction between the nuclear quadrupole moment and the crystal field gradient at the nucleus produced by the 4f ions. Both of them remove the $2I + 1$ degeneracy of the nuclear spin I ground state. Owing to the thermal population of these levels, the heat capacity at very low temperatures (between 0.02 and 0.8 K) displays a Schottky peak and it follows a T^{-2} law, as a first approximation. The electronic term is given by $C_e = \gamma T$, where the parameter γ is proportional to the density of states at the Fermi level. The lattice contribution can be expressed by the Debye term, following the low-temperature law $C_{ph} = \beta T^3$.

The magnetic contribution arises in these compounds from the removal of the $2J + 1$ degeneracy of the J ground multiplet by the CEF; the thermal evolution of the C_M term displays Schottky-type anomalies, related to the population of higher levels as the temperature increases.

3.1. Y_2Zn_{17}

This compound with a non-magnetic R ion is a Pauli paramagnet and consequently the only contributions to the heat capacity are of electronic and phonon nature. The Y_2Zn_{17} compound was measured in order to determine the phonon contribution to the total specific heat in this series of intermetallics. The experimental results are presented in a C versus T plot in figure 1. By fitting these data up to 15 K, values for γ of 9.5 mJ mol^{-1} K^{-2} and for β of 1.8×10^{-3} J mol^{-1} K^{-4} were derived. From the latter parameter we obtained a Debye temperature Θ_D of 274 K using the relation $\beta = N(\frac{12}{5})\pi^4 R(1/\Theta_D)^3$, where N is the number of atoms per formula unit. These results allow us to determine the lattice contribution for the other isostructural compounds in the series by means of the expression $C_{ph}^{R}(T) \simeq C_{ph}^{Y}(T\Theta_D^R/\Theta_D^Y)$. We have considered Θ_D proportional to $M^{-1/2}$ in all cases where M is the molar mass. The calculated Θ_D-values are collected in table 1. As can be seen in figure 1, the heat capacity of this compound does not show any anomaly in the measured temperature range, indicating the absence of any magnetic transition. The specific heats of the other compounds in this series present similar characteristics in the temperature range above 4 K.

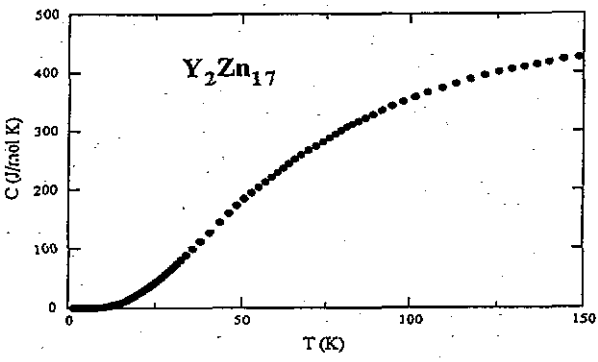

Figure 1. Experimental specific heat of Y_2Zn_{17} in a C versus T plot in the measured temperature range.

Table 1. Néel temperatures T_N and spin reorientation temperatures T_{SR} deduced from the specific-heat measurements performed in the series R_2Zn_{17}. The fourth column corresponds to the calculated Debye temperatures Θ_D.

R ion	T_N (K)	T_{SR} (K)	Θ_D (K)
Y	—	—	274
Pr	2.2	1.7	263.5
Nd	1.1	—	263
Tb	22.7	—	260.2
Dy	8.8	—	259.5
Ho	2.5	—	259
Er	1.6	1.4	258.7

3.2. Pr_2Zn_{17}

This compound does not present any anomalous behaviour in the specific heat above 3 K, being an indication of a paramagnetic state above this temperature. However, at lower temperatures we have found a very important magnetic contribution. Figure 2 shows C/T as a function of temperature for this compound. The upturn with decreasing temperature observed below 1 K arises from the nuclear contribution. A first anomaly appears at $T_N = 2.21$ K which has been ascribed to the appearance of antiferromagnetic order. The low value of the ordering temperature gives us an indication of the weakness of the magnetic exchange interaction in this compound, which points to an indirect exchange of the RKKY type. The sharp peak observed at lower temperatures in the ordered regime is possibly due to a change in the magnetic structure and is considered as a spontaneous spin reorientation transition with $T_{SR} = 1.75$ K.

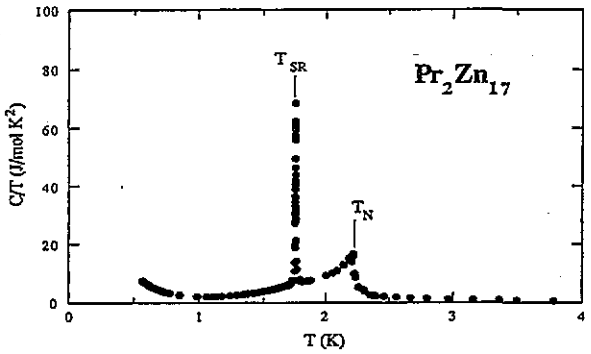

Figure 2. Experimental heat capacity of Pr_2Zn_{17} up to 4 K plotted as C/T versus T.

3.3. Nd_2Zn_{17}

A similar behaviour to that for Pr_2Zn_{17} has been found for this compound. We observed only one anomaly in the specific heat at $T_N = 1.1$ K, which is evidence of the magnetic order transition (figure 3). For this special compound we have estimated the total magnetic entropy S_M, associated with this transition, by subtracting the nuclear, electronic and phonon terms. In this case no nuclear contribution was detected above 0.3 K and in the temperature range below 4 K the phonon and electronic contributions are very small. The thermal evolution of S_M calculated after the subtraction is also plotted in figure 3. It can be seen that, after the magnetic transition, S_M attains the value $2R \ln 2$. This indicates that the doublet ground state corresponding to a Kramers ion ($J = 9/2$) is split by the exchange interactions.

3.4. Tb_2Zn_{17}

This compound presents the highest Néel temperature of the series. The heat capacity anomaly appears at 22.7 K (figure 4). A value of 28 K was derived from susceptibility measurements taking as the Néel point the temperature at which the susceptibility has a maximum (Stewart and Coles 1974). The specific-heat measurements also suggest that there might be more than one magnetic transition below T_N but the two peaks found at 6.1 and 7.2 K (see inset of figure 4) could also be due to the presence of

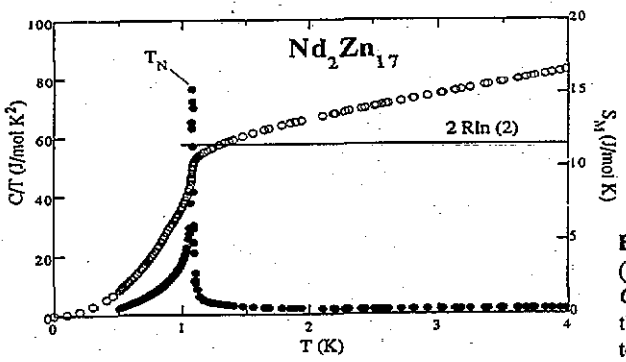

Figure 3. Experimental specific heat (●) of Nd_2Zn_{17} up to 4 K plotted as C/T versus T: ○, thermal evolution of the calculated magnetic entropy in this temperature range.

secondary phases in the sample which were not detected by the x-ray technique. As can be appreciated in figure 4, an extra contribution to the heat capacity is observed in the paramagnetic regime. This contribution corresponds to a Schottky-type anomaly associated with the population of CEF levels.

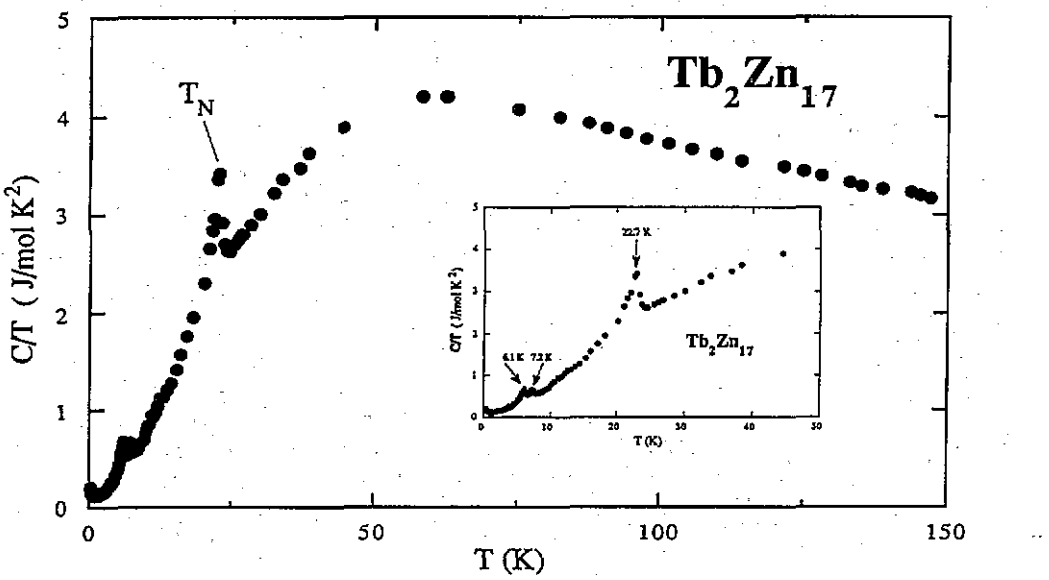

Figure 4. Temperature dependence of C/T as a function of T for Tb_2Zn_{17}. The inset shows the upturn arising from the nuclear contribution as well as the anomalies described in the text.

3.5. Dy_2Zn_{17}

Figure 5 shows the C/T versus T plot for Dy_2Zn_{17} up to 50 K. As with all the compounds in the series, this compound was measured up to 150 K but the most peculiar features appear below about 10 K. At higher temperatures the C/T versus T plot is qualitatively similar to the behaviour found in the other compounds. As shown in figure 5, Dy_2Zn_{17} orders at 8.8 K. Below T_N there is a shoulder centred

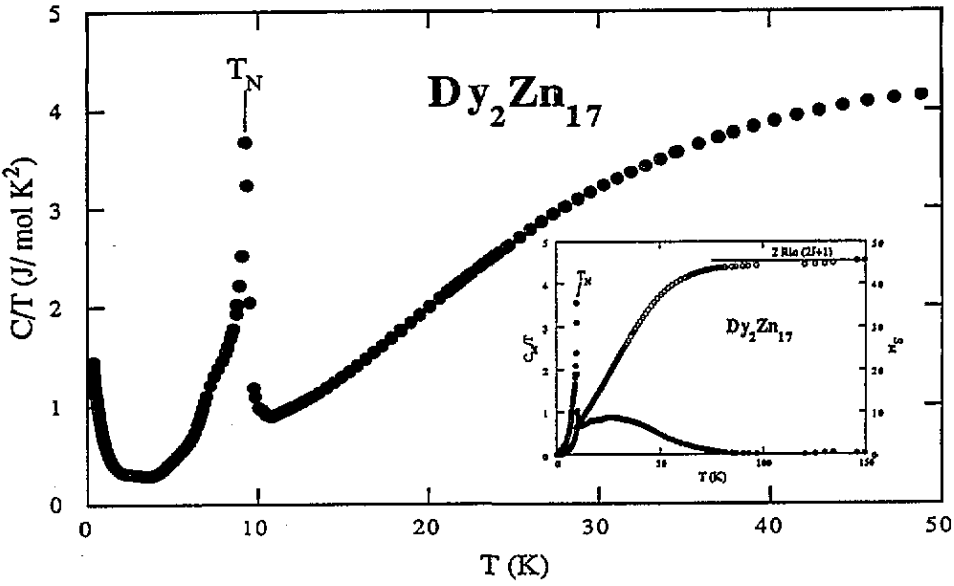

Figure 5. Experimental specific heat of Dy_2Zn_{17} in a C/T versus T plot up to 50 K. The inset shows the temperature dependence of the magnetic specific heat C_M (●) in a C_M/T versus T plot: ○, magnetic entropy as a function of temperature.

near 7.5 K, which could be associated with the thermal population of the levels split by the molecular field, which indeed is temperature dependent. Another anomaly is visible near 3 K which could be due to the presence of a secondary phase such as, for instance, dysprosium oxide. It should also be noted that the nuclear term is not negligible at least up to about 4 K. In this situation, after subtracting the non-magnetic contribution in order to estimate C_M, the derived value of the magnetic entropy involved in the magnetic transition does not reach the corresponding value for a split doublet ground state up to $T = 2T_N$. At the Néel temperature, S_M is 56% less than expected. This clearly indicates the presence of additional effects in the temperature region below 4 K. Nevertheless, at high temperatures, S_M attains the maximum $2R\ln(2J+1)$ value (see inset of figure 5). In the vicinity of 60 K, almost all CEF levels corresponding to the J ground multiplet are already populated as can be deduced from the nearly saturated thermal dependence of the magnetic entropy. This result is in close agreement with the Schottky-type anomaly observed in C_M and centred at 30 K.

3.6. Ho_2Zn_{17}

The anomaly in the specific heat indicates that the magnetic transition is centred at $T_N = 2.6$ K (figure 6). The upturn with decreasing temperature observed in the C/T versus T plot has been ascribed to the nuclear specific heat. On the other hand, the small peak observed near 3 K can be attributed to a small amount of oxides in a concentration less than 5% (Lounasmaa and Sundstrom 1966).

3.7. Er_2Zn_{17}

The total heat capacity of Er_2Zn_{17} displays two anomalies at 1.6 and 1.4 K (figure 7). According to the interpretation given in the case of the Pr compound, the first

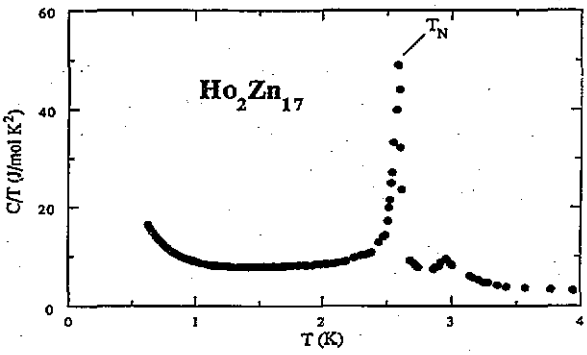

Figure 6. Temperature dependence of C/T as a function of T for Ho_2Zn_{17} in the temperature range from 0.3 to 4 K.

anomaly determines the temperature of the magnetic order transition and the pronounced anomaly in the vicinity of 1.4 K corresponds to a spontaneous spin reorientation transition. In addition, there is a small peak near 2.5 K related to the presence of a small amount of rare-earth oxides in the sample. The evaluation of C_n at low temperatures is not straightforward and it can lead to some errors in the determination of the magnetic contribution (see inset of figure 7). The magnetic entropy at T_N is close to the corresponding value for a doublet ground state. The thermal evolution of S_M indicates that nearly all CEF levels are populated in the vicinity of 40 K, where S_M tends to its maximum value $2R\ln(2J+1)$.

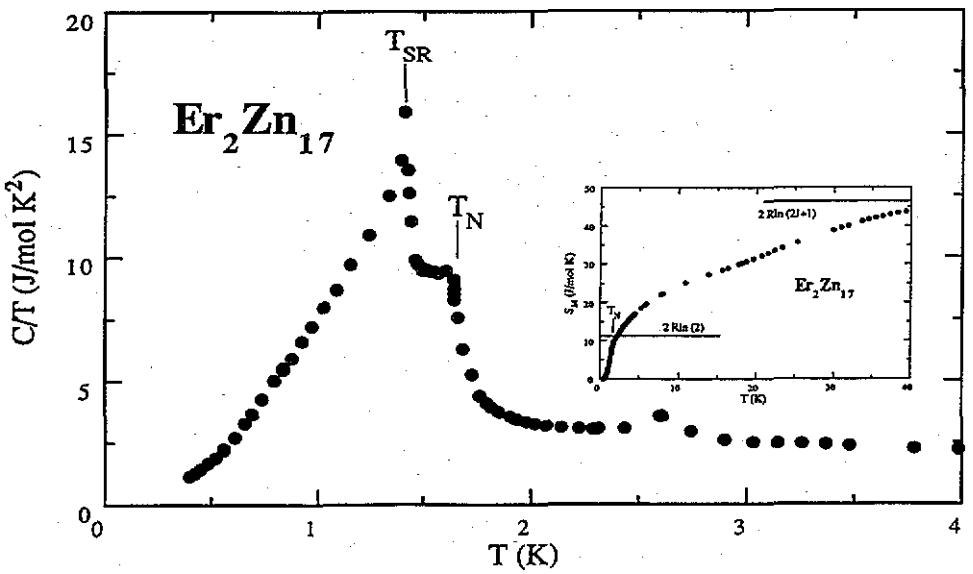

Figure 7. Experimental specific heat of Er_2Zn_{17} in a C/T versus T plot in the lowest temperature range (0.3–4 K). The inset shows the temperature dependence of the magnetic entropy in the temperature range from 0.3 to 40 K.

The results for the characteristic temperatures are summarized in table 1, where Θ_D-, T_N- and T_{SR}-values are collected. As expected in an isostructural series of compounds in which the exchange is governed by the RKKY interaction, the magnetic

order temperature follows the de Gennes law, with the maximum value of T_N expected for the Gd compound.

Summarizing, the existence of a magnetic ordered phase in the R_2Zn_{17} compounds with R ≡ Pr, Nd, Tb, Dy, Ho and Er has been established by means of specific-heat measurements. From these experimental results, the Néel temperatures have been determined. The derived values are below 3 K in all cases except for R ≡ Tb and Dy. The appearance of additional anomalies points to spin reorientation processes but further experiments are needed to confirm the origin of these anomalies. On the other hand, information about the overall CEF splitting of the spin–orbital ground state has been achieved from the experiments. A more sophisticated analysis of the magnetic contribution using a microscopic CEF formalism is under way taking into account recent neutron spectroscopy results for these compounds.

Acknowledgments

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